Pressure-induced melting of the orbital polaron lattice in $La_{1-x}Sr_xMnO_3$

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We report on the pressure effects on the orbital polaron lattice in the lightly doped manganites $La_{1-x}Sr_xMnO_3$, with $x \sim 1/8$. The dependence of the orbital polaron lattice on *negative* chemical pressure is studied by substituting Pr for La in $(La_{1-z}Pr_z)_{7/8}Sr_{1/8}MnO_3$. In addition, we have studied its hydrostatic pressure dependence in $(La_{0.9}Pr_{0.1})_{7/8}Sr_{1/8}MnO_3$. Our results strongly indicate that the hopping t significantly contributes to the stabilization of the orbital polaron lattice and that the orbital polarons are ferromagnetic objects which get stabilized by local double exchange processes. The analysis of short range orbital correlations and the verification of the Grüneisen scaling by hard x-ray, specific heat and thermal expansion data reinforces our conclusions.

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I. INTRODUCTION

The observation of a ferromagnetic insulating phase in the low-doped manganites $La_{1-x}Sr_xMnO_3$ with $x \sim 1/8$ raised a large number of studies aimed to explain the properties of this phase (e.g. 1,2,3,4,5). Several studies have shown that charge and orbital ordering phenomena are crucial to understand the obvious contradiction to the bare double exchange (DE) model, which predicts metallic behavior in case of ferromagnetic spin order. Recently, resonant x-ray diffraction succeeded to detect the formation of an orbital polaron lattice (OPL) at low temperatures, which unifies ferromagnetic and insulating properties in a natural way. It was suggested that local charge hopping processes contribute significantly to the stabilization of the orbital polarons. Further support for this conclusion was found in a recent thermodynamic study which proved the magnetic DE energy to be crucial for the stabilization of the OPL.[6]

The substitution of La by smaller Pr, i.e. the application of chemical pressure, provides a direct route to influence the balance between the various couplings that stabilize the OPL in the FMI phase. More specifically, Pr doping causes an increase of the octahedral tilt angles, thereby reducing the Mn-O-Mn bond angles and the hopping term t. It is well known that this structural change dramatically alters the relative stability of different possible phases.[11] In particular, metallic phases with delocalized charges are suppressed upon decreasing t.

In contrast to the application of negative chemical pressure, where different samples with different amounts of Pr are studied, hydrostatic positive pressure effects can be studied on a single particular compound. Here, we present data on the doping dependence of the ordering phenomena in $(La_{1-z}Pr_z)_{7/8}Sr_{1/8}MnO_3$, with y=0, 0.1, 0.25, 0.5, 0.75, and on their hydrostatic pressure dependence in $(La_{0.9}Pr_{0.1})_{7/8}Sr_{1/8}MnO_3$. Our data imply that the OPL phase is stabilized by hydrostatic pressure, i.e. upon increasing the charge mobility t. Whereas, application of negative chemical pressure yields the opposite results. The verification of the Grüneisen scaling and the analysis of short range orbital correlations reinforces our conclusions. Our study hence clearly confirms the microscopic OPL model. We mention that recently ferromagnetic correlations have been found in the charge stripe ordered phase of $La_{1.67}Sr_{0.33}NiO_4$, which might be due to local DE, too.[12] The application of chemical or external pressure might hence also affect the ferromagnetism in the doped nickelates as it is well known in the low-doped manganites.

II. EXPERIMENTAL AND RESULTS

A. Experimental

We report on measurements of the magnetisation, the specific heat, the thermal expansion, and on high energy x-ray diffraction data of $(La_{1-y}Pr_y)_{7/8}Sr_{1/8}MnO_3$ single crystals in external magnetic fields up to 16 T. The experiments were carried out on single crystals, with y=0, 0.1, 0.25, 0.5, 0.75, grown by the floating zone method.[13] The magnetisation $M(B)$ was measured with a SQUID and a vibrating sample magnetometer. Magnetization measurements under hydrostatic pressure were performed in the temperature range 4.2 - 350K using an MPMS SQUID magnetometer (Quantum Design) and a miniature piston-cylinder pressure cell made of Cu-Be alloy (PSM 100, Tetcon International). Silicon oil was used as the pressure transmitting medium. Constant magnetic fields of 0.05 T in the temperature region 50 - 250K and of 0.5 T were used in the temperature range 250 - 350 K for all measurements under pressure. The pressure at low temperature was determined by the pressure dependence of superconducting transition temperature of high purity Pb placed with the sample.

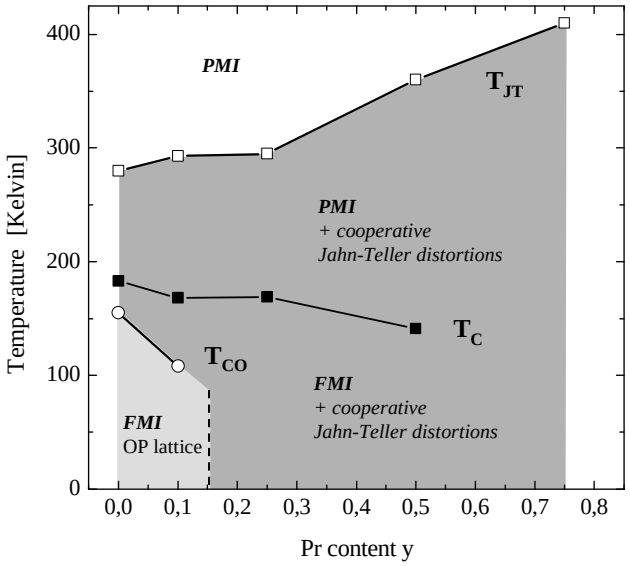

FIG. 1: Phase diagram of $(La_{1-z}Pr_z)_{7/8}Sr_{1/8}MnO_3$, based on x-ray powder diffraction as well as magnetization and resistivity measurements. The suppression of the orbital polaron lattice upon Pr doping, i.e. absence of the corresponding superstructure reflections, has been verified by high energy x-ray diffraction. T_{JT} and T_{CO} denote the transition temperatures between the indicated phases. (PMI: paramagnetic insulating; FMI: ferromagnetic insulating; FMM: ferromagnetic metallic)

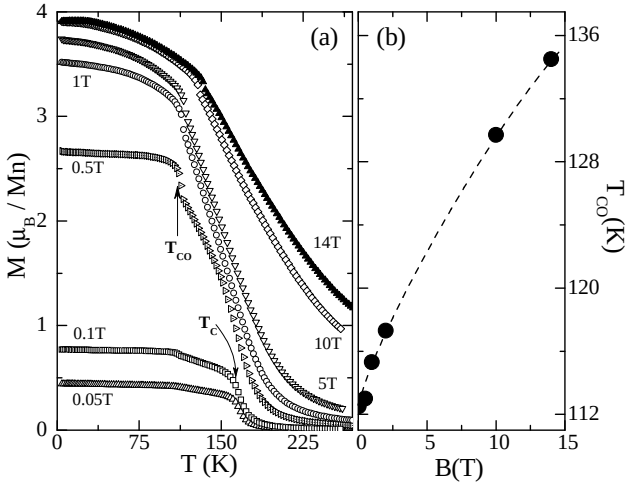

FIG. 2: (a) Magnetization vs. temperature, at different magnetic fields up to 14 T, of $(La_{0.9}Pr_{0.1})_{7/8}Sr_{1/8}MnO_3$. T_C and T_{CO} label the onset of ferromagnetic spin ordering and the OPL phase at T_{CO}. (b) Field dependence of T_{CO} as extracted from the magnetization data.

The specific heat c_p was measured using a high resolution calorimeter. Here, we have applied two different quasi-adiabatic methods, continuous heating and heating pulses.[6] For the thermal expansion studies we applied a high resolution capacitive dilatometer.[7] Hard x-ray data have been measured at the beamline BW5 at the HASYLAB, Hamburg. For experimental details see Ref. 9.

B. Pressure dependence of orbital order in $(La_{1-y}Pr_y)_{7/8}Sr_{1/8}MnO_3$

The phase diagram of $(La_{1-z}Pr_z)_{7/8}Sr_{1/8}MnO_3$ as it is presented in Fig. 1 was established by measurements of the magnetization, the specific heat, the electrical resistivity, and by x-ray diffraction data. For $y = 0$, several ordering phenomena are observed upon cooling. At T_{JT} = 270 K , a cooperative Jahn-Teller effect evolves, and ferromagnetic spin occurs at $T_C = 183$ K. Eventually, the ferromagnetic insulating phase exhibiting the orbital polaron lattice is realized below $T_{CO} = 150$ K. Upon Pr doping, i.e. by applying chemical pressure, all ordering temperatures significantly change. (1) The orbital polaron lattice is rapidly suppressed upon Pr doping. Already for $y = 0.1$ the orbital polaron lattice is considerably destabilized, while it is completely suppressed for $y = 0.25$. (2) T_C is suppressed, too, but the effect on the ferromagnetic spin ordering is less than on T_{CO}. (3) T_{JT} increases upon Pr doping, i.e. the cooperative Jahn-Teller distortions are stabilized.

In Fig. 2(a) we show the effect of the spin and the orbital ordering on the magnetization of $(La_{0.9}Pr_{0.1})_{7/8}Sr_{1/8}MnO_3$, under various applied magnetic fields up to 14 T. The effect of the magnetic field on the OPL phase is also illustrated by Fig. 2(b) which displays the field dependence of T_{CO}. At low temperatures the ferromagnetic OPL phase is realized. Upon heating, the orbital polaron lattice melts at $T_{CO} \simeq 110$ K, at which the transition is associated with a kink in the magnetization $M(T)$. This kink is visible in Fig. 2(a) e.g. at $B = 0.5$ T. The measurements in different magnetic fields imply that T_{CO} increases by 22 K upon application of $B = 14$ T [see Fig. 2(b)]. A similar behavior was observed for $La_{7/8}Sr_{1/8}MnO_3$ (see Fig. 6 of Ref. 6). When the temperature is further increased, the ferromagnetic spin order vanishes at $T_C \simeq 168$ K, and the structural Jahn-Teller phase transition is observed at $T_{JT} \simeq 296$ K.[9]

In order to study the effect of (*positive*) hydrostatic pressure on the orbital and spin ordering phenomena, we studied the temperature dependence of the magnetization of $(La_{0.9}Pr_{0.1})_{7/8}Sr_{1/8}MnO_3$ single crystals at various hydrostatic pressures up to 0.82 GPa [see Fig. 3(a)]. The data show the increase of the magnetization in the ferromagnetic metallic (FMM) and in the ferromagnetic OPL phase upon application of external hydrostatic pressure, whereas there are only minor pressure effects on the paramagnetic phase at $T > T_C$. From the data in Fig. 3(a), we have derived the pressure dependencies of the ordering temperatures T_{CO}, T_C and T_{JT}, respectively, which are displayed in Fig. 4. The data show that T_{CO} and T_C increase upon applying hydrostatic pressure, whereas T_{JT} becomes smaller. Thermodynamically, this behavior is in accordance with the fact that the volume of the unit cell shrinks at the Jahn-Teller transition and

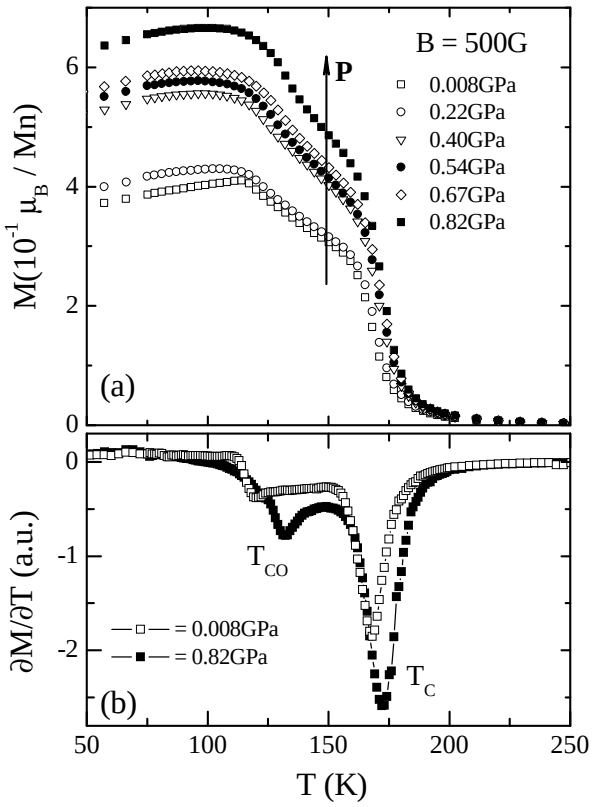

FIG. 3: (a) Magnetization vs. temperature at different external hydrostatic pressure ($B = 500\,\mathrm{G}$). (b) Derivative $\partial M/\partial T$ for lowest and highest applied pressure.

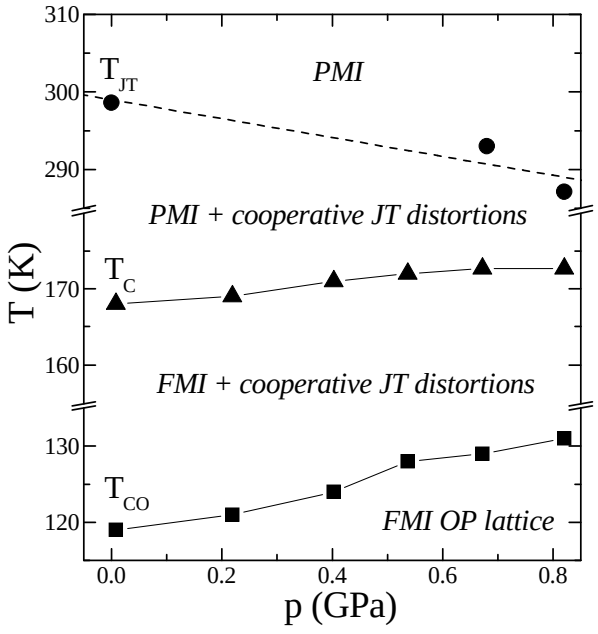

FIG. 4: Hydrostatic pressure dependencies of T_{JT}, T_{C} and T_{CO}, as extracted from the magnetization data in Fig. 3.

increases at T_{C} and T_{CO}.[9]

The fact that both the magnetization below T_{C} down to 50 K and T_{C} itself increase as a function of pressure is well understood in the framework of the DE model. Enhancement of T_{C} under hydrostatic pressure is a common trend of perovskite manganites, whereas in the single layered manganites uniaxial pressure is necessary to affect the spin ordering phenomena significantly.[15,16] In the case of $(La_{0.9}Pr_{0.1})_{7/8}Sr_{1/8}MnO_3$, the hydrostatic pressure yields an increase of t, thereby stabilizing the FMM ordered phase by enhancing the mobility of the charge carriers via the DE. Remarkably, the hydrostatic pressure dependence not only of T_{C} but also of T_{CO} is positive. This observation proves the important role of the charge hopping t and the DE for the stabilization of the OPL. The comparison of the magnetic field and the hydrostatic pressure effect on T_{CO} suggests that the application of $B = 5.6\,\mathrm{T}$ is approximately equivalent to the application of 1 GPa pressure.

At ambient pressure, the structural phase transition to the co-operative Jahn-Teller-distorted phase occurs close to room temperature, i.e. $T_{\mathrm{JT}} \simeq 296\,\mathrm{K}$, for $y = 0.1$. Under applied hydrostatic pressure, i.e. if the hopping parameter t and hence the charge mobility is increased, the cooperative JT distorted phase becomes suppressed and the dynamic JT phase is stabilized. These effects are just opposite to the chemical pressure effect upon Pr doping (y=0.1) at the La site. Note, that the effect of destabilization of the cooperative JT phase and stabilization of dynamic JT phase is observed in $La_{1-x}Sr_xMnO_3$ under applied magnetic field, too.[3]

A striking feature of our data is that, at high pressure, T_{CO} increases faster than T_{C} under pressure. This means that changes of t influence the OPL phase more effectively than the FMM phase, i.e. the DE promotes the OPL even more efficiently than the FMM phase. Faster increase of T_{CO} than T_{C} was reported under pressure in the low-doped regime around $x = 1/8$.[15] For small external pressure, however, the effect on T_{CO} is similar to that on T_{C}, which agrees with the Grüneisen scaling presented in Sec. II D.

C. Doping dependence of the OPL phase

The experimental data presented in the previous sections show that chemical (i.e. *negative* hydrostatic) pressure due to the substitution of Pr causes the destabilization of the OPL phase in $La_{7/8}Sr_{1/8}MnO_3$, whereas *positive* hydrostatic pressure yields the opposite effect. We have shown experimentally that the hopping t significantly contributes to the stabilization of the OPL. This fact provides a natural explanation for the absence of the OPL in the FMI-phase of lightly doped $La_{1-x}Ca_xMnO_3$ and $Pr_{1-x}Ca_xMnO_3$, where t is reduced due to the smaller Pr and Ca sites. For these systems there is evidence that a FMI and cooperative Jahn-Teller distorted phase exists, which corresponds to the low temperature phase of $(La_{1-z}Pr_z)_{7/8}Sr_{1/8}MnO_3$ with $y \geq 0.25$.

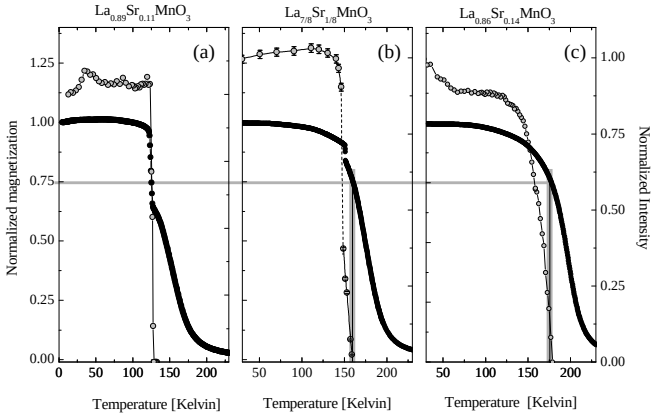

FIG. 5: Comparison between the temperature dependencies of the magnetization measured in an external field of 0.5 Tesla and the intensities of the superlattice reflections determined by HXS for $x = 0.11$, 1/8 and 0.14. The data sets have been normalized to the respective low temperature values. The superlattice reflections only occur, if the normalized magnetization increases above 0.75 (gray lines).

The relevance of the charge hopping t for the stabilization of the OPL in $La_{1-x}Sr_xMnO_3$ is further supported by the measurements shown in Fig. 5. In this figure, the temperature dependencies of the magnetization measured in an external field of 0.5 Tesla and the intensities of the superlattice reflections measured by high-energy x-ray diffraction are compared for $x = 0.11$, 1/8 and 0.14. The magnetic entropy in the FMM-phase between T_C and T_{CO} decreases with increasing doping level; i.e. the magnetic disorder in this phase is largest for $x = 0.11$ and decreases towards $x = 0.14$. According to the double exchange (DE), the charge hopping in the FMM-phase of $La_{0.89}Sr_{0.11}MnO_3$ is considerably suppressed, as the magnetic disorder is large. At the same time, the intensity of the superstructure reflection corresponding to the OPL vanishes completely in the FMM-phase [Fig. 5(a)] of this compound. The increase of the strontium doping to $x = 1/8$ leads to a reduction of the magnetic disorder in the FMM-phase as compared to the $x = 0.11$ sample. In this case, the superstructure reflection corresponding to the OPL is already observed in the FMM-phase [Fig. 5(b)], revealing the presence of short range OPL order in the FMM-phase of $La_{7/8}Sr_{1/8}MnO_3$. Similarly, the HXS-measurements on $La_{0.86}Sr_{0.14}MnO_3$ indicate the presence of short range OPL correlations above T_{CO}, too [cf. Fig. 5(c)].

A remarkable observation concerns the temperatures which mark the onset of the short range correlations. As indicated in Fig. 5, the onset of the short range correlations in the samples with $x = 1/8$ and $x = 0.14$ corresponds in both cases to the temperature where the magnetization reaches about 75 % of its saturation value. For $x = 0.11$, the magnetization never reaches the 75 % value (gray horizontal line in Fig. 5) in the FMM phase of $x = 0.11$; i.e. the magnetic disorder is too large to allow for the short range OPL order.

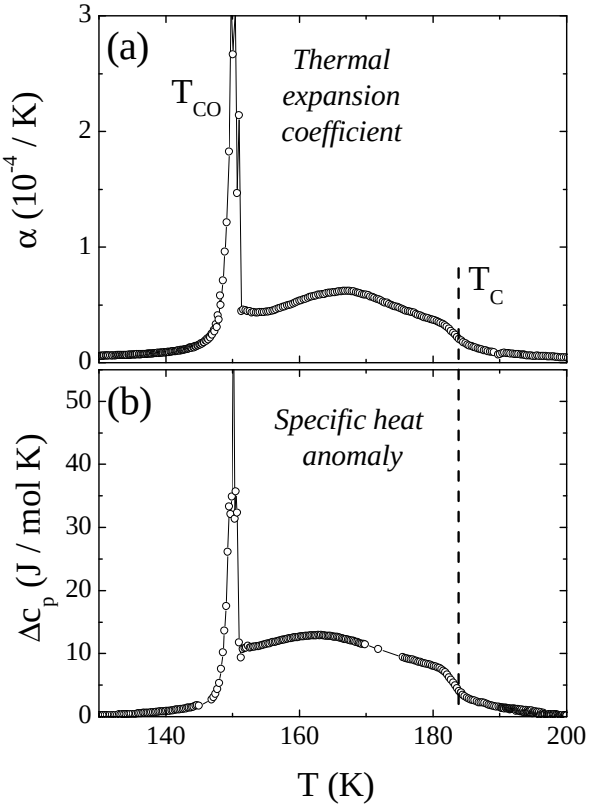

FIG. 6: (a) Thermal expansion coefficient and (b) specific heat anomaly of $La_{7/8}Sr_{1/8}MnO_3$.

D. Grüneisen scaling for $La_{7/8}Sr_{1/8}MnO_3$

The results presented above clearly show that the formation of the OPL phase and of the FMM phase is based on a common energy scale which is given by the hopping parameter t. Hence, the pressure dependencies of the relevant energy scale for the ordering phenomena must agree, since it is the same energy scale. This can be checked experimentally by the verification of the Grüneisen scaling, i.e by measuring the anomalous contributions to the specific heat c_p and to the thermal expansion coefficient α. If the Grüneisen scaling is fulfilled, both quantities are proportional. Quantitatively, the Grüneisen relation reads

$$\frac{\alpha}{c_p} = \frac{1}{V} \left. \frac{\partial \ln \epsilon}{\partial p} \right|_T , \qquad (1)$$

with ϵ being the relevant energy scale of the respective ordering phenomenon, i.e. in the case at hand $\epsilon = \epsilon(t)$. We hence studied the specific heat and the thermal expansion coefficient of $La_{7/8}Sr_{1/8}MnO_3$. From both data we subtracted the phonic contribution, which was estimated from the specific heat data as is explained e.g. in Ref. 6. The resulting anomalous contributions to the specific heat and to the thermal expansion are shown in Fig. 6. As has been shown earlier[3,6], the formation

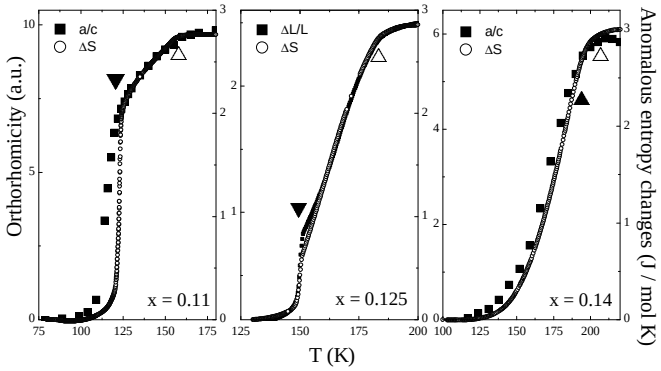

FIG. 7: Temperature dependence of the orthorhombicity a/c and of the anomalous entropy changes for $La_{1-x}Sr_xMnO_3$, with $x = 0.11$ and $x = 0.14$. For comparison, the integrated data of Fig. 6, i.e. the anomalous length and entropy changes for $x = 1/8$, are also shown. Full (open) triangles mark T_{CO} (T_C).

of the FMM phase causes a jump of the specific heat at T_C and a large peak is associated with the onset of the OPL phase at T_{CO}. In addition, there is a regime of anomalous entropy changes at $T_{CO} \leq T \leq T_C$. All these features are visible in the thermal expansion data in Fig. 6(a), too. There is a peak at T_{CO}, a jump at T_C and a regime of anomalous length changes in the whole FMM phase. The data hence clearly prove very similar temperature dependencies of c_p and α. This observation implies that both ordering phenomena at T_{CO} and at T_C have the same pressure dependence, which reinforces our conclusions drawn above. In addition, this is also true for the entropy changes in the whole temperature regime $T_{CO} \leq T \leq T_C$.

This conclusion does not only hold for $La_{7/8}Sr_{1/8}MnO_3$ but also for $x = 0.11$ and 0.14. This is illustrated by Fig. 7, which shows that the Grüneisen scaling is valid in its integral form for these compositions. The figure presents the temperature dependencies of the orthorhombicity a/c and of the anomalous entropy changes $\Delta S = \int c_p/TdT$.

III. CONCLUSION

Our results show that charge hopping processes are essential to stabilize the OPL in $La_{1-x}Sr_xMnO_3$. However, since the OPL leads to macroscopically insulating behavior, these hopping processes take place on a local scale, i.e. within the orbital polarons. To be more specific, the orbital polarons are ferromagnetic objects which get stabilized by local DE processes.[17] The pressure effects enhance the local DE processes by increasing t and hence lead to the stabilization of OPL at low temperature. The magnetic disorder and the suppression of the orbital polaron lattice created by the Pr (y=0.1) doping is counterbalanced by the external pressure for stabilizing the orbital polaron lattice at low temperatures. Our analysis of the short range orbital correlations and the verification of the Grüneisen scaling reinforces our conclusions regarding the relevance of t and DE for the formation of the OPL.

Acknowledgments

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